human cancers and mutation breeding of crops and microbes by means of ion-beam technology. However, the underlying mechanism for the energetic particle induced biological effects is still elusive because the interacting system involves radiolysis of different biomolecules such as DNA, proteins, sugar and lipids, and moreover, there are cross-correlations among these varied substances due to their interactions and signal transductions in living cells. A new trend of research is therefore to investigate the interaction between energetic particles and organisms with consideration of the entire cellar micro-environment and the entangled processes occurring in a whole cell, and to scrutinize the changes of cellular structure and compositions on the micro-scale and also monitor the dynamic and kinetic processes for the interactions. In this context, it is very useful and powful to apply micro-spectral imaging technology such as FTIR and Raman confocal microscopy because it can provide not only good time and spatial resolution, but also non-invasive measurement. In this work, we utilized the high spatial resolution FTIR and Raman microscopy to study the cellular changes of some model microbes and cells by mapping and monitoring the fingerprint bands of the cellular components such as lipids, carbohydrates, polyunsaturated fatty acids, proteins and nucleic acids under the irradiation of energetic particles. Correspondingly, the cell activity, the intracellular content of ROS, the level of MDA and GSH, the activity of CAT and SOD were measured to explain the biological effect induced by energetic particles. This work is supported by NSFC (No. 10975152, No. 11175204), CAS Innovative Project (KJX2-YW-N34-1) and Hundred Talents Program of CAS, China.

3001-Pos Board B771

Simulating the Amide I IR Signal of a Peptide in Solution using a Classical Implicit Water Approximation

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Behavior of the amide I IR signal of peptides has been the object of much study because it can provide valuable information about the environments and conformations of peptides in solution. Numerous models have been proposed to predict the amide I band shape, the most successful of which may have limited utility in studying dynamic processes due to high computational cost. Here a new, simple method is employed to predict the effects that the aqueous environment and side chains have on the shape of the amide I IR signal for a polypeptide in water. Using GEPOL to generate a solute cavity, apparent charges at the solvent accessible surface are generated considering a conductor like response from the solvent to partial charges on atoms (AMBER, or CHARMM). Potentials on the atoms in amide groups resulting from the surface charges and from the side groups are then used along with an electrostatic potential map to predict how the amide I signals are perturbed from gas phase signals. Effects of cavity size and atomic partial charges on the integrity of predicted band shapes are examined. The method gives results comparable to much more computationally intensive methods.

3002-Pos Board B772

Measuring Moments of Protein Conformation Distributions using Infrared Spectroscopy

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Infrared spectroscopy is often used to characterize the concentration and secondary structures of proteins in a variety of static and dynamics samples. Our work develops new methods to compare the structure, dynamics and function of nearly identical protein samples, in order to help characterize bio-similar protein therapeutics. We have developed a method to describe protein conformational variations around the average molecular values. By comparing the moments of the protein structural distributions and amide hydrogen/deuterium exchange methods, we explore the relationships between protein stability and dynamics. Examples include lysozyme and albumin in solution, cytochrome c interacting with lipid membranes of varying net-negative surface charge density, and bacteriorhodopsin during its photocycle.

3003-Pos Board B773

Isotope-Edited FT-IR Spectra of Isotopmers of Helical Hexamers of Alpha-Aminoisobutyric Acid

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Isotope-edited FT-infrared spectra of the Amide I region of hexamers of alpha-aminoisobutyric acid (Z-Aib_6-OtBu) have been collected in order to explore the effects of $^{13}C{=}O$ enrichment on the FT-IR spectra in the conformational context of 3_{10} helices. Oligomers of Aib are known to adopt predominantly 3_{10} helical structures, even at short peptide lengths. The Amide I band is sensitive to the details of peptide secondary structure, but the competency of this band to distinguish between alpha- and 3_{10} helical secondary structure remains an open question. The 3_{10} helix is shorter than an alpha-helix of the same number of residues and exhibits an i to i+3 hydrogen bonding pattern, instead of an i to i +4 pattern of the alpha-helix. These differences bring amide oscillators of a 3_{10} helix slightly closer in space and in shorter periodicity of hydrogen-bonding partnership as compared to an alpha-helix. We have collected infrared spectra of isotopomers of hexamers of Aib (e.g., Z-Aib-Aib-Aib-Aib-Aib-Aib-OtBu, Z-Aib*-Aib-Aib*-Aib-Aib-Aib-OtBu, and Z-Aib*-Aib*-Aib-Aib-Aib-Aib-OtBu, Aib* = ^{13}C enrichment at *C=O) in dichloromethane (a nonpolar aprotic solvent) and methanol (a polar, protic solvent) to examine the effects of carbon-13 enrichment on the spectra. Differences among the spectra of peptide isotopomers enriched with one or two ^{13}C labels will be examined, detailing the effects of coupling between pairs of ^{13}C-labeled Amide I oscillators.

3004-Pos Board B774

Under Pressure: Measuring Desolvation of Model α-Helical Peptides

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Model helical peptides have been shown to unfold with temperature, but are stabilized with increased pressure [1-3]. In these peptides, as pressure increases, the solvent environment becomes ordered allowing for an increase of the helical content of the peptide. Our work investigates hydration of the peptide backbone using both temperature and pressure as modifying conditions. The synthetic peptide sequence, $(AAAAK)_3$-AAAAY is well-characterized and ideal for the study of helix properties[3]. To measure the coupling of pressure and temperature, Fourier transform infrared spectroscopy (FTIR) monitors the perturbations in the secondary structure via the amide I' band. FTIR is a sensitive technique for detecting changes in hydrogen bonding and has been used for the estimation of amide photon exchanging with the solvent. Pressure on the peptide is applied using a manually manipulated Diamond Anvil Cell (DAC). Isotopically labeled residues within the peptide have been exploited for probing local interactions due to the shift of the heavier masses of the labeled residues to a lower frequency compared to the global ^{12}C amide I band around 1633 cm^{-1}. Our goal is to compare the location of isotopically edited alanines and the ability to remain desolvated with increasing pressure and temperature. With this technique, it was found that alanines proximal to the lysines were protected from solvent hydrogen interactions due to side chain shielding in the model sequence.

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3005-Pos Board B775

Dependence of Plant Cell Wall Composition and Structure on Cellulose Synthase-Like Knock Out Mutant

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Plant cell walls are a complex mixture of polysaccharides, proteins and the phenolic polymer lignin that have been recently targeted as possible sources of fermentable sugars for the production of biofuels. The development of a biomass-based biofuels industry is partly dependent on genetic engineering and breeding next generation crops containing, among other traits, easily extractable cell wall sugars. Thus, a better understanding of how plants synthesize, deposit and modify their cell walls is necessary for the selection of traits important for biofuel crop improvement. The identification of plants with altered cell wall composition or structure can prove useful in the discovery of novel genes involved in the biosynthesis and modification of the cell wall.
The CELLULOSE SYNTHASE-LIKE 6 (CSL6) gene has been recently shown to mediate the biosynthesis of mixed-linkage glucan (MLG), a cell wall polysaccharide that is thought to be necessary for cell wall expansion in the primary cell wall of young seedlings. A detailed analysis of a loss-of-function MLG rice mutant has been recently conducted revealing surprising results. Though the mutant showed a 99% reduction of MLG content, the rice clsf6 knock out mutant showed only a slight decrease in growth compared to wildtype. The cell wall properties of both mutant and wild type were determined via biochemical and various spectroscopic (Fourier Transform Mid-Infrared spectroscopy)

analyses. We found that not only was the composition of the cell wall dramatically altered, but the overall structure of the cell wall was affected demonstrating the flexibility of plant polysaccharide organization to compensate for changes within the cell wall.

3006-Pos Board B776

FTIR Study of Temperature and pH Effects on Amino Acid Side-Chains

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Analysis of protein amide I IR bands can be complicated by absorption of side-chain groups. Side-chain IR spectra have been previously studied at acidic (pH ~2.3) and neutral (pH ~7) conditions, which take account of the protonated and deprotonated states of the carboxylic groups, but only at room temperature. It is expected that in thermal denaturation experiments these side-chain absorptions will change in both frequency and intensity with respect to temperature. This will additionally convolute the Amide I spectra unless corrected for. In order to attain these corrections an equilibrium study of temperature effects on amino acid side-chain absorptions has been conducted at both pH's for the amino acids glutamine, glutamic acid, asparagine, aspartic acid, and arginine. Experiments were carried out in a 1mM deuterated phosphate buffer. Deuterated amino acids were dissolved (1mg Amino Acid/60μL Buffer) in the buffer and scanned using a Bruker Tensor 27 FTIR. Samples were heated via a software controlled water bath from 0C to 87C, with scans taken every 3C. The collected temperature and pH dependent side-chain absorptions were normalized, to published room temperature data, and fit to pseudo-Voigt functions. It was found that both frequency and intensity exhibit linear changes with respect to temperature, though direction and magnitude varied between amino acids. These known shifts can thus be accounted for in the Amide I spectra analysis of proteins.

3007-Pos Board B777

A Co-Translationally Insertable Donor-Acceptor Pair for the Real Time Study of Vibrational Energy Transfer in Proteins

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Vibrational energy flow in biological macromolecules can be nicely studied by ultrafast pump-probe spectroscopy, given that suitable chromophors for injecting and tracking energy flow are present. Here we present a study on a new donor-acceptor pair consisting of two artificial aminoacids, with an azulene chromophore as a ''donor'', that can be excited at 600 nm and injects vibrational energy into the peptide or protein investigated. An azide chromophore is serving as an ''acceptor'', which can be monitored at 2100 cm-1 to track energy flow in the system. These labels combine a set of very favourable properties for the study of IVR in biological macromolecules. Co-translational incorporation of each of the labels into proteins has been demonstrated in the form of beta-(1-azulenyl)-L-alanine and L-azido-homo-alanine. To investigate the performance of the azulene-azide donor-acceptor pair, we designed a model peptid (Aaa-Tyr-Asn-Aha-Gly) inculding both chromophores and additional protein marker modes, such as tyrosine, asparagine and glycine providing the c-terminal carboxyl. We performed Vis-pump IR-probe experiments on the peptide, covering the range from 1200 cm-1 to 2120 cm-1. While in azulene-containing monomers, studied for comparison, the infrared signals reached their maximum within 2ps, we found for the peptide a pronounced correlation between the through-bond distance of a vibrating group from the azulene chromophore and the time until the IVR induced signal of this group becomes maximal. The signal of the azide band of our ''acceptor'' azido-homo-alanine is the dominating contribution at 9-10 ps. Even over a distance of four residues, it reaches a signal size comparable to the total amide I intensity of the peptide. In the light of the presented results the application of the azulene-azide donor-acceptor pair for IVR studies in proteins appears very promising.

3008-Pos Board B778

Molecular Structure and Stability of Phospholipid Monolayers Probed by Vibrational Sum Frequency Spectroscopy (VSFS)

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Deposited and floating monolayers of phospholipids are commonly used as model systems for biological membranes, since their complex structure make spectroscopic investigations difficult. In this research, the surface specific technique Vibrational Sum Frequency Spectroscopy (VSFS) was applied to investigate the molecular structure, packing properties, and hydrating water of Langmuir-Blodgett monolayers of *1,2-distearoyl-sn-glyerco-phosphatidylcholine* (DSPC, 18:0 PC), its deuterated analog (18:0 PC-d83), and *1,2-distearoyl-sn-glyerco-phosphatidylserine* (DSPS, 18:0 PS) deposited on CaF_2 substrates at a surface pressure of 35 mN/m. The CH and CD stretching regions, the water region, and the lower wavenumber region, containing phosphate, ester, carboxylate, and amine signals, thus partly covering the fingerprint region, were probed to obtain a complete map of the molecules. All phospholipids formed well ordered, stable monolayers. Probing the water region revealed significant differences in hydration of the different headgroups. The tilt angle of the aliphatic chains relative to the surface normal was estimated to 4° to 10° based on orientational analysis of the antisymmetric methyl stretch, and the result of a qualitative orientational analysis of the ester C=O groups was consistent with the tilt angle of the aliphatic chains.

Additionally, the stability of Langmuir monolayers of 18 PC with various degrees of unsaturation in the aliphatic chains was studied *in situ*. To monitor the degradation of the phospholipids the time dependent change of the Langmuir monolayer area at constant surface pressure and the SF intensity of the vinyl CH stretch were measured. While monolayers of fully saturated phospholipids formed stable, well ordered films at the water surface, phospholipids containing unsaturated aliphatic chains showed a significantly lower stability and rapid degradation. Nitrogen purging of the ambient air inhibited the breakdown, attributed to spontaneous degradation by oxidation mediated by reactive species in the air.

3009-Pos Board B779

Digital Parallel Acquisition in Frequency Domain for the Characterization of Tissue Spatial Heterogeneities

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Near-infrared (NIR) (650-1000 nm) optical properties of turbid media can be accurately quantified noninvasively using methods based on diffuse reflectance or transmittance, such as frequency domain photon migration (FDPM). For instance, Diffuse Optical Spectroscopy (DOS) is a noninvasive technique that is commonly used to provide biochemical information on hemoglobin, bulk lipids and water concentration by NIR tissue absorption and scattering. DOS does not require exogenous contrast, and rapidly provides quantitative, functional information about tumor biochemical composition. Conventional FDPM techniques are based on white-light steady-state (SS) measurements and the acquisition of frequency-domain (FD) data at several wavelengths using laser diodes, to measure broadband NIR scatter-corrected absorption spectra of turbid media. These techniques are limited by the number of wavelength points used to obtain the FD data. We developed a new method to improve the acquisition of optical parameters of the examined tissues, based on digital parallel acquisition in FD. With our system, both FD and SS measurements are performed using a super-continuum white laser alone. Moreover, the white laser allows a continuous scan of frequencies in the spectral medical window, thus providing additional wavelength information. At each wavelength, we extract what we refer to be as the tissue phasor. The estimated absorption and scattering coefficients are obtained by fitting phase shift and demodulation with a mathematical model for a semi-infinite geometry. In previous works we showed the possibility of non-invasively predicting chemotherapy response prior to treatment based on biomarkers obtained from tumor spatial heterogeneities of spectral features measured using a conventional DOS instrument. With the method here presented, we expect to improve the characterization of breast tumor spatial heterogeneities and the prediction of chemotherapy outcome. Work supported by NIH-P41-RR003155.

Computational Methods II

3010-Pos Board B780

Cross-Talk and Information Transfer in Mammalian and Bacterial Signaling

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In both mammalian cells and bacteria, simple phosphorylation circuits play a very important role in cellular function. Bacteria have hundreds of two-component signaling systems that involve phosphotransfer between a receptor kinase and a response regulator. In mammalian cells a similar pathway is the crucial TGF-beta signaling pathway, where extracellular levels of TGF-beta family ligands lead to activation of receptors that phosphorylate Smad proteins, which in turn activate many genes. In TGF-beta signaling the multiplicity of external ligands begs the question as to how cells distinguish signals coming from different extra-cellular ligands, but transduced through a small set of Smads. Here we use information theory with stochastic simulations of simple networks to address this question. We find that when signals are transduced through the same Smad, the cell cannot distinguish between different levels